

1992

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Mark Draganjac

University of Illinois at Urbana-Champaign

Thomas B. Rauchfuss

University of Illinois at Urbana-Champaign

Arnold L. Rheingold

University of Delaware

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Recommended Citation

Draganjac, Mark; Rauchfuss, Thomas B.; and Rheingold, Arnold L. (1992) "Model for the CO Poisoning of Hydrodesulfurization Catalysts. Synthesis and Structure of $\{\text{Ru}(\text{CO})[\text{PPh}_2\text{SC}_{12}\text{H}_7)]_2\text{Cl}_2\} \cdot 2\text{CH}_2\text{Br}_2$," *Journal of the Arkansas Academy of Science*: Vol. 46 , Article 1.

Available at: <http://scholarworks.uark.edu/jaas/vol46/iss1/1>

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MODEL FOR THE CO POISONING OF HYDRODESULFURIZATION CATALYSTS. SYNTHESIS AND STRUCTURE OF $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\} \cdot 2CH_2Br_2$.

MARK DRAGANJAC and THOMAS B. RAUCHFUSS
School of Chemical Sciences
350C Noyes Lab, Box 21, 505 S. Mathews Ave.
Urbana, Illinois 61801

ARNOLD L. RHEINGOLD
Department of Chemistry
University of Delaware
Newark, Delaware 19716

ABSTRACT

The treatment of $\{Ru[(PPh_2SC_{12}H_7)]_2Cl_2\}$ with CO at ambient conditions results, after work up, in the isolation of the monocarbonylated species $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\}$, I. Crystals of I ($C_{51}H_{38}Br_4Cl_2OP_2RuS_2$; F.W. = 1284.6) are triclinic; $P\bar{1}$; $a = 11.587(3)$, $b = 13.010(4)$, $c = 17.309(4)$ Å, $\alpha = 93.32(2)^\circ$, $\beta = 106.51(2)^\circ$, $\gamma = 91.29(2)^\circ$; $Z = 2$; $V = 2495(1)$ Å³; $d_{calc} = 1.709$ g cm⁻³; λ (Mo K α) = 0.71073 Å, $\mu = 37.7$ cm⁻¹; $R = 0.0748$; $R_w = 0.0714$ for 4141 unique reflections. The geometry about the Ru(II) center is pseudooctahedral, with the phosphine ligands in the *trans* configuration. The Ru-S bond distance is 2.425(3) Å.

INTRODUCTION

The hydrodesulfurization (HDS) of fossil fuels is the industrial process for the removal of sulfur from fossil fuel feedstocks (eq. 1).



The resulting hydrotreated product is then suited for the sulfur sensitive cracking and reforming catalysts downstream. Hydrotreated fuels are also desirable because they generate fewer acid rain precursors upon combustion.

The molecular basis of the HDS process involves the activation of the crude feedstock in hydrogenolysis by metal catalysts. Molybdenum-based catalysts are widely used, although recent work has shown that ruthenium-based systems are even more active (Pecoraro and Chianelli, 1981; Chianelli *et al.*, 1984; Harris and Chianelli, 1984). The organosulfur components targeted by HDS consists of thiols, thioethers and thiophenes, especially benzo- and dibenzothiophenes (DBT). In order to elucidate the nature of the substrate-catalyst interactions we sought to prepare ruthenium complexes of DBT-derivatives. In 1984 we reported the first such complex in the form of $\{Ru[(PPh_2SC_{12}H_7)]_2Cl_2\}$ where $PPh_2SC_{12}H_7$ is 4-diphenyl-phosphinoDBT, a P-S chelating ligand (Bucknor *et al.*, 1984). As this was the first S-bound DBT complex, we are interested in probing its reactivity in order to evaluate the lability of the Ru-S bonds. We selected CO as the competing ligand since it was known that CO poisons HDS catalysts (Lombardo *et al.*, 1980).

MATERIALS AND METHODS

The compound $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\}$, I, was prepared by purging a dichloromethane solution of $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\}$ with CO gas. The resulting solution was concentrated and chromatographed on silica gel, eluting with dichloromethane. The yellow band was evaporated to give yellow microcrystals. Anal. calcd. for $C_{49}H_{34}Cl_2OP_2RuS_2$: C, 62.82; H, 3.63; Cl, 7.59. Found: C, 63.34; H, 3.79; Cl, 7.66. IR (CH_2Cl_2 soln): $\nu_{CO} = 1988$ cm⁻¹. ³¹P NMR ($CDCl_3$): 50.63, 41.56, 20.64, 11.62 ppm; $S_A = 45.38$, $S_B = 16.84$, $J = 366$ Hz. The elemental analysis was performed at the School of Chemical Sciences, University of Illinois. ³¹P{¹H} NMR spectra were obtained on an NSF-250 spectrometer.

Single crystals were grown by the slow diffusion of diethyl ether into a solution of I in dibromomethane. A yellow crystal, 0.30 x 0.35 x 0.36 mm, was mounted on a glass fiber. Intensities were measured on a Nicolet R3m/μ diffractometer using the ω scan technique, scan speed varied 5-20 deg. min⁻¹. The unit cell was determined from the least-squares analysis of angle data for 25 reflections with $19 < 2\theta < 26^\circ$. Data were collected to $(\sin \theta)/\lambda$ of 0.56 Å⁻¹, $\pm h$, $\pm k$, $\pm l$. Three standard reflections collected every 197 reflections decreased < 2% over data collection. Corrections to the intensity data for L_p effects, absorption (empirical) and for decay

were applied. A total of 7785 reflections was measured with 7374 unique ($R_{int} = 1.86\%$) and 4141 observed reflections with $F_o < 4\sigma(F_o)$. The structure was solved by direct methods which provided the location of one heavy atom (Ru) and four initially confusing peaks of apparent Z greater than P, S, or Cl that proved to be the Br atoms of the two positionally disordered molecules of CH_2Br_2 . The remaining nonhydrogen atoms were obtained from subsequent difference Fourier syntheses. The final refinement model incorporated a rigid, planar hexagonal constraint to the P-bound phenyl rings, and the C-Br distances were collectively refined to a common value of 1.86(1) Å. All nonhydrogen atoms were refined with anisotropic temperature factors, and the hydrogen atoms were included as idealized, isotropic contributions, but were not refined. For a total of 567 parameters, $R = 0.0748$, $R_w = 0.0714$, $S = 1.407$. Final $(\Delta\sigma)_{max} < 0.09$ eÅ⁻³ on the final difference map. All computations used SHELXTL (5.1) software (Nicolet Corp., Madison, WI).

RESULTS

Crystal data are given in Table 1. The structure of $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\} \cdot 2CH_2Br_2$, I, is seen in Fig. 1. Atomic and equivalent thermal parameters are given in Table 2. Selected bond distances and angles can be seen in Table 3.

Table 1. Crystal Data for $\{Ru(CO)[(PPh_2SC_{12}H_7)]_2Cl_2\}$

Formula	$C_{51}H_{38}Br_4Cl_2OP_2RuS_2$
MWT	1284.6
Space group	triclinic $P\bar{1}$
a	11.587(3) Å
b	13.010(4) Å
c	17.309(4) Å
α	93.32(2)°
β	106.51(2)°
γ	91.29(2)°
V	2495(1) Å ³
Z	2
d_{calc}	1.709 g cm ⁻³
μ (MoK α)	37.7 cm ⁻¹
MoK α	0.71073 Å
Observed reflections	4141
R/R_w	0.0748/0.0714

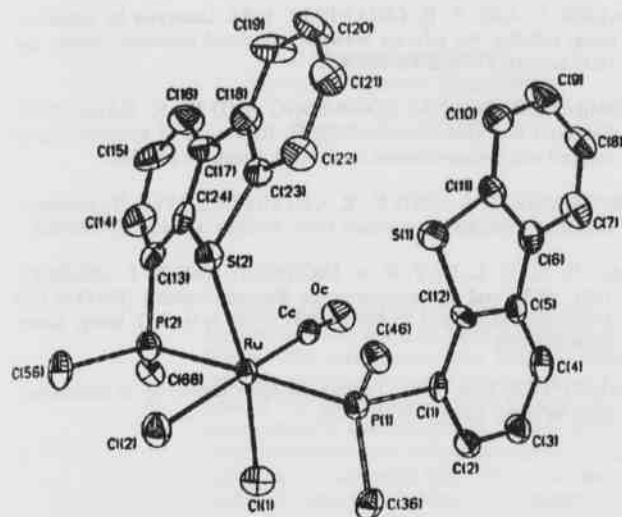


Figure 1. Structure of $[\text{Ru}(\text{CO})(\text{PPh}_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2]$ showing atom labeling scheme. The hydrogen atoms have been omitted and the phenyl rings are shown as ipso atoms for clarity. Thermal ellipsoids drawn by ORTEP represent 35% probability surfaces.

DISCUSSION

The addition of CO results in the breaking of one of the Ru-S bonds in $[\text{Ru}(\text{CO})(\text{PPh}_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2]$ and causes a rearrangement of the phosphines from the all *cis* configuration to a *trans* geometry, as seen in the structure of I (Fig. 1). One of the phosphine ligands remains chelated

Table 2. Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\text{CO})(\text{PPh}_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2]$.

Atom	x	y	z	Ueq
Ru	2568(1)	2756(1)	2120(1)	28(1)
Cl(1)	2194(3)	4558(3)	1920(2)	50(1)
Cl(2)	4723(3)	3186(3)	2730(2)	47(1)
Br(1)	964(2)	8808(1)	4941(2)	132(1)
Br(2)	-386(2)	6846(2)	3894(1)	121(1)
Br(3)	6179(1)	6427(2)	3020(1)	141(1)
Br(4)	4429(2)	6866(2)	1321(1)	139(1)
P(1)	2207(3)	3050(3)	3420(2)	33(1)
P(2)	2864(3)	2566(3)	796(2)	39(1)
S(1)	338(3)	851(3)	3038(2)	47(1)
S(2)	3139(3)	984(3)	2112(2)	38(1)
Co	880(13)	2450(10)	1628(7)	37(5)
Oo	-17(9)	2340(8)	1353(5)	55(4)
C(1)	591(10)	3032(9)	3305(6)	31(4)
C(2)	23(11)	3976(10)	3287(7)	40(5)
C(3)	-1240(11)	3984(10)	3089(7)	47(5)
C(4)	-1945(11)	3091(11)	2930(7)	50(6)
C(5)	-1411(10)	2153(9)	2920(7)	37(5)
C(6)	-1984(10)	1120(10)	2724(7)	43(5)
C(7)	-3199(11)	823(12)	2533(8)	58(6)
C(8)	-3363(12)	-206(11)	2339(8)	61(6)
C(9)	-2721(15)	-948(13)	2360(9)	72(7)
C(10)	-1503(12)	-791(11)	2573(8)	49(6)
C(11)	-1156(11)	350(10)	2754(7)	41(5)
C(12)	-136(10)	2093(8)	3109(6)	30(4)
C(13)	2401(11)	1237(10)	471(7)	42(5)
C(14)	1835(14)	800(12)	-316(8)	57(7)
C(15)	1391(14)	-195(11)	-454(8)	64(7)
C(16)	1439(13)	-794(12)	185(9)	62(7)
C(17)	1976(12)	-420(9)	985(7)	43(5)
C(18)	2061(11)	-888(10)	1740(7)	47(5)
C(19)	1701(14)	-1874(11)	1857(9)	64(7)
C(20)	1927(14)	-2170(11)	2638(9)	67(7)
C(21)	2468(12)	-1519(11)	3288(8)	56(6)
C(22)	2812(11)	-515(11)	3178(8)	49(6)
C(23)	2611(11)	-198(9)	2399(7)	37(5)
C(24)	2472(11)	581(10)	1087(7)	44(5)
C(25)	3541(7)	4950(6)	3842(4)	42(5)
C(26)	3982(7)	5831(6)	4348(4)	54(6)
C(27)	3639(7)	6012(6)	5052(4)	55(6)
C(28)	2856(7)	5312(6)	5251(4)	64(7)
C(29)	2416(7)	4431(6)	4744(4)	55(6)
C(30)	2759(7)	4249(6)	4040(4)	38(5)

Table 2. Continued...

Atom	x	y	z	Ueq
C(41)	2224(6)	1830(7)	4740(5)	45(5)
C(42)	2813(6)	1266(7)	5388(5)	58(6)
C(43)	4009(6)	1013(7)	5494(5)	70(7)
C(44)	4616(6)	1323(7)	4951(5)	59(6)
C(45)	4026(6)	1887(7)	4302(5)	43(5)
C(46)	2830(6)	2140(7)	4197(5)	39(5)
C(47)	3086(11)	1907(8)	678(6)	91(9)
C(48)	6282(11)	2074(8)	684(6)	152(15)
C(49)	6785(11)	3075(8)	781(6)	146(15)
C(50)	6085(11)	3910(8)	871(6)	136(12)
C(51)	4888(11)	3743(8)	864(6)	79(8)
C(52)	4389(11)	2741(8)	768(6)	51(6)
C(53)	2427(7)	3299(7)	-729(5)	66(7)
C(54)	1744(7)	3747(7)	-1416(5)	70(7)
C(55)	634(7)	4151(7)	-1428(5)	67(7)
C(56)	208(7)	4107(7)	-753(5)	65(6)
C(57)	891(7)	3639(7)	-66(5)	48(6)
C(58)	2001(7)	3255(7)	-54(5)	42(5)
C(59)	807(11)	7383(11)	4797(6)	130(11)
C(60)	4627(5)	6348(20)	2325(7)	202(17)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Selected Bond Distances (\AA) and Angles ($^\circ$) for $[\text{Ru}(\text{CO})(\text{PPh}_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2] \cdot 2\text{CH}_2\text{Br}_2$

Ru-Cl(1)	2.409(3)	Ru-S(2)	2.425(3)
Ru-Cl(2)	2.454(3)	Ru-Co	1.92(1)
Ru-P(1)	2.413(3)	Co-Oo	1.02(1)
Ru-P(2)	2.413(4)	Ru...S(1)	4.232(3)
Cl(1)-Ru-Cl(2)	90.5(2)	Cl(2)-Ru-Co	179.1(4)
Cl(1)-Ru-P(1)	87.7(1)	P(1)-Ru-P(2)	176.7(1)
Cl(1)-Ru-P(2)	89.3(1)	P(1)-Ru-S(2)	103.0(1)
Cl(1)-Ru-S(2)	168.6(1)	P(1)-Ru-Co	90.2(4)
Cl(1)-Ru-Co	88.9(4)	P(2)-Ru-S(2)	80.1(1)
Cl(2)-Ru-P(1)	90.5(1)	P(2)-Ru-Co	88.5(4)
Cl(2)-Ru-P(2)	90.8(1)	S(2)-Ru-Co	94.8(4)
Cl(2)-Ru-S(2)	85.7(1)	Ru-Co-Oo	176(1)

through the thiophenic sulfur. The Ru-S bond distance of 2.425(3) \AA is slightly longer than the two comparable distances in $[\text{Ru}(\text{P}(\text{p-tolyl})_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2]$: Ru-S₁, 2.343(5); Ru-S₂, 2.402(5) \AA (Bucknor *et al.*, 1984). The pyramidal nature of the coordinated sulfur is evident by the angle defined by Ru-S₂-(C₁₇C₁₈ midpoint). This angle of 131.8° in I compares favorably with the two independent angles (132.0 and 130.1°) in $[\text{Ru}(\text{P}(\text{p-tolyl})_2\text{SC}_{12}\text{H}_7)_2\text{Cl}_2]$ (Bucknor *et al.*, 1984). In the $[\text{Ru}(\text{hCp})(\text{PPh}_3)_2\text{BPh}_4]$ complex, the Ru-S-(C-C midpoint) angle is 126° and the Ru-S bond distance is 2.408(1) \AA (Draganjac *et al.*, 1985). The pyramidal nature of the thiophenic sulfur upon coordination has also been observed in the $\text{CpFe}(\text{CO})_2\text{DBT}^+$ (Goodrich *et al.*, 1987) and $\text{Cp}^*\text{IrCl}_2\text{DBT}^+$ (Rao *et al.*, 1991) complexes. Angelici (1990) and Rauchfuss (1991) have reviewed structural aspects of thiophene coordination.

Refluxing acetonitrile solutions of I in the presence of trimethylamine oxide for 24 hrs did not result in decarbonylation. This fact and the ease of thiophene displacement by CO may be relevant to the CO poisoning of the HDS catalysts (Lombardo *et al.*, 1980).

SUPPLEMENTAL MATERIAL

Anisotropic Thermal Parameters, Positional Parameters for the Hydrogen Atoms, Bond Lengths and Angles, and Structure Factor Tables (25 pages) are available from the authors upon request.

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